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Donor and Acceptor Properties of the Chromium Tricarbonyl Substituent in Benzylic and Homobenzylic Anions, Cations, and Radicals

Craig A. Merlic,* Bruce N. Hietbrink, and K. N. Houk*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569

Merlic@chem.ucla.edu

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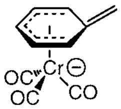
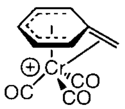
Both benzylic cations and anions are strongly stabilized by chromium tricarbonyl complexation, while benzylic radicals are largely unaffected. Density functional theory calculations were performed on primary, secondary, and tertiary benzylic species to explore the effect of substitution on the stabilizing ability of the chromium tricarbonyl moiety. Complexed 1-indanyl species were also examined to elucidate the effect of conformational restraint. It was found that the strong stabilization of benzylic anions and the slight destabilization of benzylic radicals by chromium tricarbonyl are insensitive to skeletal changes. Chromium-complexed benzylic cations, however, are highly sensitive to changes in the organic framework, with increased substitution or constriction of conformational mobility eroding the effect of the metal. 2-Indanyl species were also examined to study the effect of the chromium tricarbonyl fragment on homobenzylic species. It was found that the metal fragment stabilizes distant anions by field and inductive effects and cations by a direct interaction of the metal with the cationic carbon. Homobenzylic radicals, however, do not interact with the chromium tricarbonyl moiety and suffer a slight inductive destabilization.

Introduction

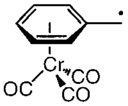
Chromium tricarbonyl complexation leads to strong stabilization of both benzylic anions and cations,[1] and generation of these species and trapping in a stereoselective fashion is critical in many synthetic applications.[2] Recent theoretical studies of chromium tricarbonyl complexes of benzyl anion, cation, and radical, **1a**−**c**, demonstrated that the stabilization of benzylic species is achieved through geometric distortions allowing the transition metal to participate, yet maintain an 18-electron configuration.[3] Anionic complex **1a** has a pentadienyl anion fragment η^5-coordinated to the metal and an exocyclic π bond inclined away from the chromium center. In cationic complex **1b**, the exocyclic π bond bends down and coordinates to the metal, providing an η^7-coordinated 18-electron complex. In radical complex **1c**, on the other hand, there is no significant distortion of the exocyclic carbon−carbon bond either toward or away from the metal center. Calculations indicate that two-thirds of the spin density remains on the benzylic carbon.[3b] The complex closely resembles a simple η^6 arene complex of the metal (an 18-electron configuration), and there is no extra stabilization imparted to the benzylic radical due to the chromium tricarbonyl moiety.



1a



1b



1c

The previous theoretical studies only examined primary benzylic intermediates.[3] Many experimental systems, in particular synthetic applications involving stereochemistry, do not involve primary intermediates such as these.[4] To expand our understanding of chromium stabilization of benzylic intermediates, we examined theoretically, using density functional theory calcula-

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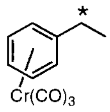
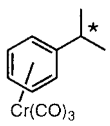
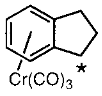
tions, the chromium tricarbonyl complexes of secondary and tertiary anions, cations, and radicals **2a**−**c** and **3a**−**c**, to see if the trends observed for primary species hold for more substituted molecules. We also explored the effect of constraining the reactive intermediates in a cyclic system, **4a**−**c**, and the effect of the chromium tricarbonyl moiety on homobenzylic intermediates **5a**−**c**.



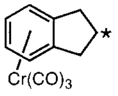
2a-c



3a-c



4a-c



5a-c

a * = ⊖ **b** * = ⊕ **c** * = •

Background

Chromium tricarbonyl complexation dramatically increases the acidity of benzylic protons,[5] which allows for selective functionalization of the benzylic position of chromium arene complexes.[5a] In conformationally restricted systems, only the protons anti to the metal are removed by bases, and subsequent trapping of the intermediate anions also occurs from the sterically more accessible anti face.[5b] Deprotonation and trapping thus proceeds with retention of configuration.[5c] Diastereotopic α protons in planar chiral arenes can be selectively deprotonated due to conformational preferences,[5d] and achiral substrates can be treated with chiral bases to enantioselectively functionalize the benzylic position.[5e] Some aspects of the effect of chromium tricarbonyl on distant anionic centers have also been examined. Chromium complexation lowers the pK_a of benzoic acid from 5.68 to 4.77, and it lowers the pK_a of phenylacetic acid from 5.64 to 5.02.[6] From these results it is inferred that the metal exerts an electron-withdrawing effect similar to that of a nitro group.

Somewhat surprisingly, the chromium tricarbonyl moiety also stabilizes benzylic cations.[7] Holmes, Jones, and Pettit found that chromium complexation of benzyl chloride increases the rate of solvolysis by a factor of 10^5.[7a] The rate of hydrolysis of chromium-complexed cumyl chloride is also increased relative to the uncomplexed cumyl chloride, but only by a factor of 28.[7b] As with benzylic anions, the intermediate chromium-complexed benzylic cations do not freely rotate about the exocyclic C−C bond,[3,7c] so the metal can be used as a source of stereocontrol. These carbocations can be trapped by a wide variety of nucleophiles[7d−g] which approach from the face of the arene anti to the chromium center.[7h] Thus, solvolysis of acyclic substrates occurs with net retention of configuration.[7i] Chromium complexation also accelerates solvolysis reactions β to arenes and provides stereocontrol.[8] As we reported previously, this is due to direct interaction of chromium d electrons with the forming carbocation.[9]

While they have not received as much attention as anionic and cationic complexes, there is a growing body of evidence that chromium tricarbonyl bound benzylic radicals are intermediates in a number of highly stereoselective reactions.[4f,10] (Benzaldehyde)chromium tricarbonyl reacts with samarium(II) diiodide forming a ketyl radical which dimerizes with a high degree of stereocontrol.[10a] The chromium tricarbonyl complex of 1-indanone forms a ketyl radical that can be trapped with methyl acrylate from the face anti to the bulky chromium tricarbonyl, giving a single diastereomeric product.[4f,10b,c] Other benzylic radicals complexed to chromium tricarbonyl have also been described.[10d−k]

Given the complexity of these and other synthetically relevant systems, a deeper understanding of the reactive intermediates derived from the parent structures **1a**−**c** is needed.

Methods

All calculations were performed using the Gaussian 94 and Gaussian 98 programs.[11] Geometry optimizations utilized the B3LYP method[12] and the LANL2DZ basis set.[13] All optimized structures were characterized by frequency analysis. Single

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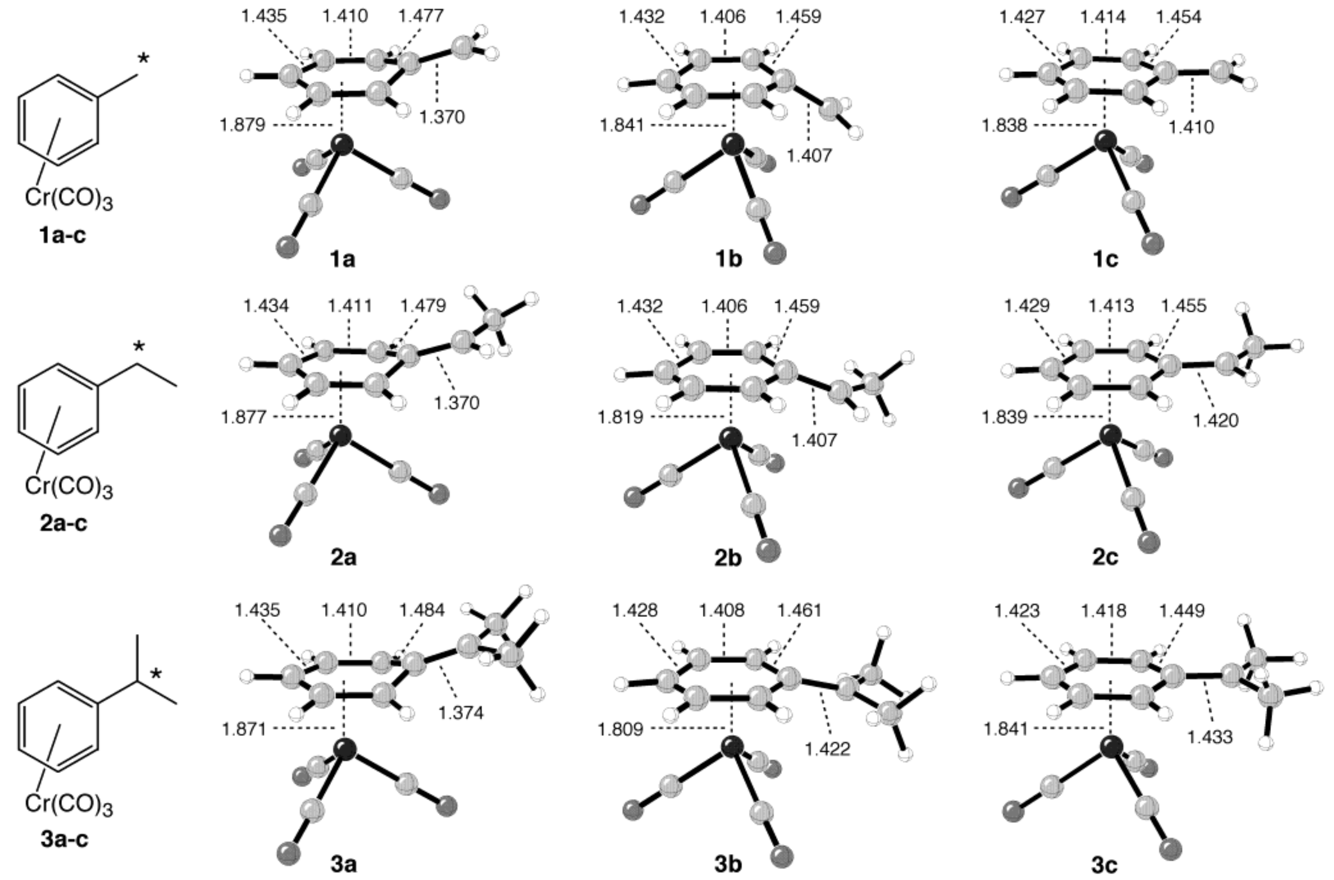


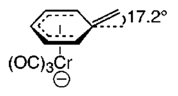
Figure 1. (U)B3LYP/LANL2DZ optimized geometries of chromium tricarbonyl complexed benzylic anions (a), cations (b), and radicals (c). Selected distances in angstroms.

point energies were computed at the B3LYP/DZVP2+ level[14] and include zero point corrections (unscaled) from frequency calculations at the B3LYP/LANL2DZ level of theory. Previous studies have shown this to be an appropriate level of theory for chromium tricarbonyl complexed arenes.[3a,9]

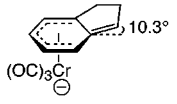
Results

Acyclic Benzylic Species. Fully optimized geometries were located for chromium complexes with primary (**1a**−**c**), secondary (**2a**−**c**), and tertiary (**3a**−**c**) anions, cations, and radicals (Figure 1).[15] The overall geometric features of the secondary and tertiary benzylic complexes **2a**−**c** and **3a**−**c** are similar to those previously reported for primary benzylic complexes **1a**−**c**.[3] However, a few important differences do arise.

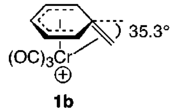
In all three anionic complexes, **1a**, **2a**, and **3a**, the chromium tricarbonyl tripod is syn eclipsed with respect to the benzylic anion (Figure 1). Bond lengths vary by less than 0.01 Å among the primary, secondary, and tertiary anions. In each case the exocyclic $C_{ipso}-C_{\alpha}$ bond is inclined away from the metal center—by 17.2° relative to the arene plane for both primary anion **1a** and secondary anion **2a**, and by 19.2° for tertiary anion **3a**.



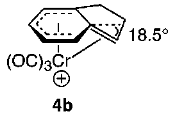
1a



4a



1b



4b

There is greater variation among the three cationic complexes **1b**, **2b**, and **3b** (Figure 1). In each case the chromium tripod is anti eclipsed with respect to the benzylic cation. Bond lengths are also similar among the complexes and to the anionic complexes except for the $C_{ipso}-C_{\alpha}$ bond, which is longer. The greatest difference is in the inclination of the exocyclic $C_{ipso}-C_{\alpha}$ bond relative to the arene plane. In all three cases this bond is inclined toward the metal, but the magnitude of the distortion from planarity decreases as the substitution of the cation increases. This bond is inclined from the arene plane by 35.3° in primary cation **1b**, by 21.8° in secondary cation

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(15) Geometries for compounds **6**−**23** are provided in the Supporting Information.

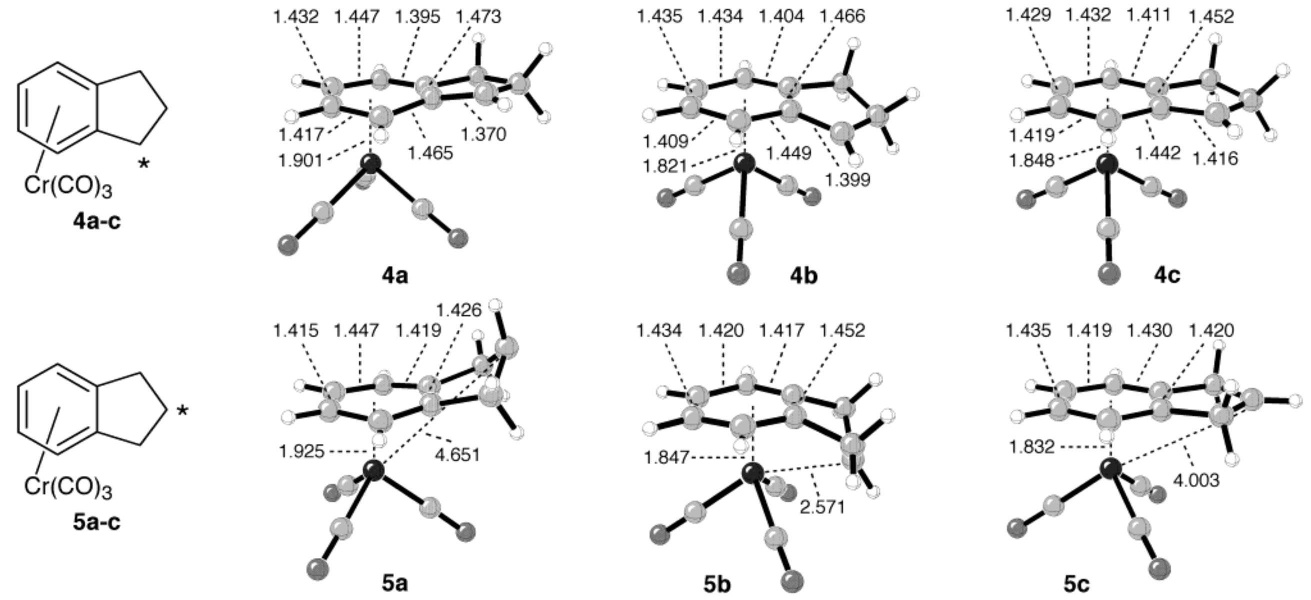


Figure 2. (U)B3LYP/LANL2DZ optimized geometries of chromium tricarbonyl complexed 1- and 2-indanyl anions (a), cations (b), and radicals (c). Selected distances in angstroms.

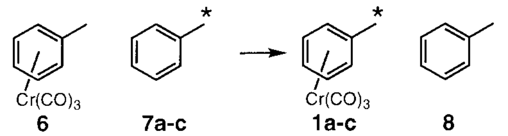
2b, and by only 12.7° in tertiary cation **3b**. There is a concomitant lengthening of the Cr$-$C$_\alpha$ distance from 2.940 Å in **1b** to 3.144 Å in **3b**.

The three radical complexes **1c**, **2c**, and **3c** are quite similar to each other (Figure 1). All three have anti eclipsed chromium tricarbonyl fragments, and bond lengths within the arene rings vary by less than 0.01 Å. The exocyclic C$_{ipso}$$-C_\alpha$ bond is nearly coplanar with the arene ring in each case (tilted away from the metal by only 1.9° in **1c**, 1.5° in **2c**, and 1.6° in **3c**). There is a steady lengthening of the exocyclic C$_{ipso}$$-C_\alpha$ bond upon substitution of the benzylic position, presumably to minimize steric interactions between the *ortho* hydrogens and the methyl substituents. This may also reflect a decreasing reliance on resonance delocalization for stabilization of the benzylic radical.

The energetic consequences of chromium complexation on primary, secondary, and tertiary anions, cations, and radicals are summarized in homodesmotic[16] eqs 1, 2, and 3.[17] The benzylic substitution pattern has essentially no effect on the stabilization of benzylic anions and radicals. Chromium complexation stabilizes primary, secondary, and tertiary anions by 33 kcal/mol, and it slightly destabilizes primary, secondary, and tertiary radicals by about 1 kcal/mol. Cation stabilization, on the other hand, varies greatly with benzylic substitution. Chromium stabilizes primary benzyl cation **1b** by 12.0 kcal/mol, but this effect is dramatically reduced by more than half by methyl substitution, with a stabilization of 5.1 kcal/mol for secondary cation **2b**. For the tertiary cation the effect of the metal is reduced further, with **3b** stabilized by only 1.7 kcal/mol relative to uncomplexed cation **13b**.

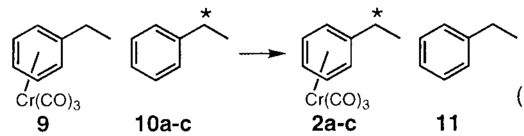
1-Indanyl Species. Next, we turned to indanyl substrates to explore the effects of geometric constraints on the structure and energetics of the complexes. Fully optimized geometries were located for the chromium tricarbonyl complexes of 1-indanyl anion, cation, and radical **4a**$-$**c** (Figure 2).[15]

Chromium tricarbonyl complexation affects the geometry of anionic complex **4a** relative to the noncomplexed anion (Figure 2).[15] The bond between the anionic center and the arene ring is slightly shortened upon complexation, to the same extent as seen in parent anion **1a**. The chromium tricarbonyl fragment of **4a** is syn eclipsed with respect to the anionic center, as was observed in **1a**. The characteristic tilt of the bond to the anionic center away from the metal is 10.3° relative to a plane defined by the pentadienyl fragment in **4a**. This is only 60% of the tilt



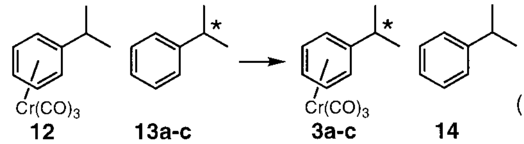
(eq 1)

a * = ⊖ ΔE = -33.4 kcal/mol
b * = ⊕ ΔE = -12.0 kcal/mol
c * = • ΔE = +0.8 kcal/mol



(eq 2)

a * = ⊖ ΔE = -33.3 kcal/mol
b * = ⊕ ΔE = -5.1 kcal/mol
c * = • ΔE = +0.8 kcal/mol



(eq 3)

a * = ⊖ ΔE = -33.3 kcal/mol
b * = ⊕ ΔE = -1.7 kcal/mol
c * = • ΔE = +0.6 kcal/mol

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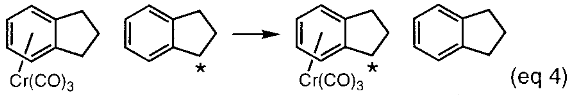
[16] George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Theor. Chim. Acta* **1975**, *38*, 121$-$129.

[17] Slight differences between the energetics reported in eq 1 and those reported in ref 3a are due to the inclusion of zero point corrections in the present work.

seen in the parent benzyl anion, **1a**[3] and acyclic secondary anion **2a**. In this complex, as well as the other complexes examined herein, the bonds within the arene ring are lengthened by up to 0.025 Å relative to noncomplexed species.[15] This lengthening has also been observed experimentally.[18]

The geometry of 1-indanyl cation complex **4b** also reflects the effect of metal complexation (Figure 2). The partial double bond between the cationic center and the arene ring is lengthened by 0.006 Å relative to the uncomplexed cation.[15] The chromium tricarbonyl tripod is anti eclipsed in relation to the cationic center, and the metal is slightly closer to the arene ring than in the parent neutral complex **16**. The benzylic cation is inclined toward the metal center in **4b**, but only by 18.5°. This is 52% of the angle seen in the parent benzyl cation **1b**,[3] and 85% of the angle seen in acyclic secondary cation **2b**.

Unlike the anionic and cationic complexes, bond lengths within the 1-indanyl radical complex **4c** are relativly unaffected by chromium complexation (Figure 2). There is a slight lengthening of the arene ring bonds, as seen in other chromium complexes.[18] Like cationic complex **4b**, the chromium tricarbonyl moiety of **4c** is anti eclipsed. The most important structural feature in the radical system, though, is the lack of bending of the benzylic center relative to the metal. As with benzylic radical complexes **1c**,[3] **2c**, and **3c**, the bond from the benzyl radical to the arene ring is nearly coplanar with the pentadienyl fragment.



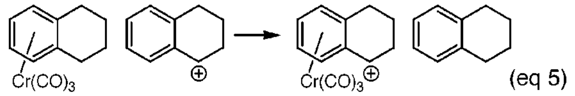
16 **15a-c** **4a-c** **17** (eq 4)

a * = ⊖ ΔE = -31.7 kcal/mol

b * = ⊕ ΔE = -0.3 kcal/mol

c * = • ΔE = +1.6 kcal/mol

Homodesmotic[16] eq 4 reveals that the chromium tricarbonyl moiety stabilizes the 1-indanyl anion by 31.7 kcal/mol compared to 33.3 kcal/mol for the acyclic secondary system **2a** (eq 2). However, the cation is stabilized by only 0.3 kcal/mol (eq 4), compared to the 5.1 kcal/mol stabilization of **2b** (eq 2). Although both **2b** and **4b** are secondary cations, the conformational limitations of the indanyl ring system in **4b** remove the ability of the metal to strongly interact with the cationic center. A very similar effect is seen in the homologous tetralinyl cationic system (eq 5).[15] The effect of chromium complexation upon 1-indanyl radical stability (eq 4) is quite similar to that seen in the conformationally unrestricted system. (1-Indanyl radical)chromium tricarbonyl **4c** is destabilized by 1.6 kcal/mol, compared to a 0.8 kcal/mol destabilization of **2c** (eq 2).



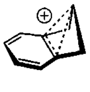
18 **19** **20** **21** (eq 5)

ΔE = -1.1 kcal/mol

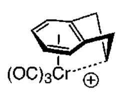
2-Indanyl Intermediates. The effect of chromium complexation upon homobenzylic reactive intermediates was also explored to examine long-range effects. Additionally, this complements our more specific study of benzonorbornenyl cations.[9a] Fully optimized geometries were located for the chromium tricarbonyl complexes of 2-indanyl anion **5a**, cation **5b**, radical **5c** (Figure 2) in addition to the noncomplexed species.[15]

The 2-indanyl anion distorts upon chromium complexation by tilting the homobenzylic position away from the metal center (Figure 2). The chromium tricarbonyl tripod of **5a** is eclipsed with respect to the anionic center, as in **1a**, **2a**, and **3a**.

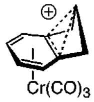
The 2-indanyl cation **22b** is a nonclassical cation[19] wherein the homobenzylic position is inclined toward the arene ring to allow interaction between the empty p orbital and the arene π system. As shown in our previous communication,[9a] chromium complexation dramatically changes this. In complex **5b** the cationic center preferentially interacts with the chromium. This is evidenced by a relatively short Cr−C distance of 2.571 Å and a rehybridization of the C2 to direct the p-like orbital toward the metal.



22b



5b



23

We were unable to locate any alternative minimized geometry for the cationic complex in which the cationic center is involved in a nonclassical interaction as in **22b**. In geometry **23**, the homobenzylic carbon is computationally constrained to a distance of 2.050 Å from the two arene *ipso* carbons.[15] However, geometry **5b**, with direct chromium interaction with the cationic center, is 13.6 kcal/mol more favorable than constrained geometry **23**, with nonclassical stabilization of the cationic center. This energy difference is very similar to the previously reported 15.0 kcal/mol difference between syn and anti chromium tricarbonyl complexes of 7-benzonorbornenyl cation.[9a]

In 2-indanylchromium tricarbonyl radical **5c** there is no interaction between the metal and the radical center (Figure 2). The organic fragment of **5c** maintains the planarity of the uncomplexed system **22c**.

The energetic effect of chromium complexation on reactive species at the homobenzylic position were elucidated by homodesmotic eq 6. Surprisingly, chromium tricarbonyl stabilizes the homobenzylic anion by 19.6 kcal/mol. Both Coulombic interactions between the partially positive chromium and the anionic carbon and the inductive withdrawing effect of the chromium tricarbonyl moiety serve to stabilize the anion, since resonance effects are not possible. The Coulombic component of this stabilization would be expected to be strongly attenuated by solvation. This result suggests that the large stabilization of anions at the benzylic position includes field

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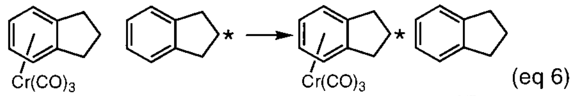
[18] Le Magueres, P.; Lindeman, S. V.; Kochi, J. K. *Organometallics* **2001**, *20*, 115−125.

[19] (a) Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc.* **1949**, *71*, 2953. (b) Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183−4184. (c) *Carbonium Ions;* Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III. (b) Brown, H. C.; Schleyer, P. v. R. *The Nonclassical Ion Problem;* Plenum Press: New York, 1977. (c) Brown, H. C. In *The Transition State*; Chemical Society Special Publication 16; Chemical Society: London, 1962; pp 140−158, 174−178. (d) Wilt, J. W.; Chenier, P. J. *J. Org. Chem.* **1970**, *35*, 1571−1576.

(through-space) and inductive (through-bond) components in addition to the previously discussed[3] resonance component. Chromium stabilizes the homobenzylic cation by direct coordination, but only by 4.3 kcal/mol. This small, but significant, stabilization is in part due to the fact that noncomplexed **22b** is already stabilized nonclassically, and metal complexation in **5b** is merely replacing the nonclassical stabilization with d orbital electron participation. As with benzylic radicals, chromium exerts a slight (1.3 kcal/mol) destabilizing effect on radicals at the homobenzylic position.



16 **22a-c** **5a-c** **17** (eq 6)

$\mathbf{a}\ * = \ominus \qquad \Delta E = -19.6$ kcal/mol

$\mathbf{b}\ * = \oplus \qquad \Delta E = -4.3$ kcal/mol

$\mathbf{c}\ * = \cdot \qquad \Delta E = +1.3$ kcal/mol

Discussion

Neither substitution at the benzylic position nor restriction of the conformational freedom of benzylic anions significantly diminishes the stabilizing effect of the chromium tricarbonyl moiety. Secondary and tertiary anions **2a** and **3a** are stabilized to the same extent as primary anion **1a**. Even though the benzylic position of compound **4a** can only tilt away from the metal by 10.3°, compared to 17.2° in **1a**, there is still a 31.7 kcal/mol stabilization of the negatively charged center. This is only slightly less than the 33.4 kcal/mol stabilization calculated for **1a**. Also, the inductive withdrawal of electron density from the anionic center is not significantly affected by restricted geometry about the benzylic center. Probably the most surprising and dramatic result is the sizable stabilization of complexed homobenzylic anions through field and inductive effects, though the former effect would be decreased in solution.

A much more dramatic structural effect is seen in the cationic systems. Secondary and tertiary cations **2b** and **3b** receive much less stabilization from the chromium moiety than primary cation **1b**, due to the fact that the alkyl substituents are electron releasing and thus stabilizing. This is an instance of the "tool of increasing electron demand:"[20] since secondary and tertiary cations are stabilized, they do not require as much stabilization from the metal. This is consistent with previous studies, in which the rate of solvolysis of primary substitutents was increased by a factor of 10^5 by chromium[7a] while that of tertiary substitutents was only enhanced by a factor of 28.[7b] In the 1-indanyl cation complex **4b**, the stabilizing effect of the metal would be expected to be reduced relative to **1b**, because **4b** is secondary, as is seen for **2b**. However, tying the cationic center of **4b** into a ring limits its tilt toward the metal to 18.5°, only about half of the 35.4° distortion seen in parent benzyl cation **1b**. This decrease in overlap between the metal d orbitals and the cationic center nearly eliminates the cationic stabilization seen in **1b**, or even **2b**. These calculations suggest that in reactions where a chromium-bound benzylic cation is conformationally restricted, or where the cation is tertiary, the metal is primarily playing a steric role rather than one of direct participation.

Benzylic radicals **2c**, **3c**, and **4c** and homobenzylic radical **5c** are structurally unaffected by the presence of the chromium substituent, and none are significantly stablized relative to the noncomplexed analogues. In fact, all are slightly destabilized by up to 1.6 kcal/mol. This destabilization may be due to inductive electron withdrawl by the chromium tricarbonyl moiety on the electron-deficient radical center. These results are in accord with our previous study on the chromium complexed benzyl radical.[3a] Further, the results are also in line with the experimental results of Newcomb wherein aryl substituents had little electronic effect on the stability of benzyl radicals.[21]

Two additional structural changes between the parent neutral complexes and the reactive species can be generalized. First, the rotational orientation of the chromium tricarbonyl tripod is silmilar to that observed in X-ray crystal structures.[1d] That is, the syn eclipsed conformation is favored for electron rich substituents such as anions or alkoxy groups, while the anti eclipsed conformation is favored for electron-withdrawing or -deficient substituents such as cations, radicals, or carbonyl groups. These preferences are due to favorable orbital interactions between the metal and the arene ring.[3a,22] Second, subtle but significant shifts occur in the position of metal complexation. In the benzyl anion complexes the metal moves from the centroid of the aromatic ring away from the anionic substituent and adopts an η^5-coordination. In contrast, the metal moves from the centroid toward the cationic substituent in the benzyl complexes in order to facilitate η^7-coordination.

Conclusions

Density functional theory calculations indicate that the strongly stabilizing effect of chromium tricarbonyl on benzylic anions is insensitive to alterations of the hydrocarbon framework, whether these be alkyl substitution or constraint of the inclination of the benzylic position. In addition to resonance effects on the anion, there is also a strong inductive withdrawing effect of the metal that is not affected by substitution. The strong stabilization of benzylic cations, on the other hand, is extremely sensitive to skeletal alterations. Substituents that stabilize cations remove the need for interaction with the metal. The stabilizing effect of the chromium also depends on a close Cr−C interaction, such that constraining the system to reduce the orbital overlap between the metal and the benzylic position effectively removes the stabilization. The structure and stability of chromium complexes of benzylic radicals are relatively unchanged by changes in the organic fragment, and in all cases there is a slight destabilization due to complexation.

Chromium tricarbonyl also exerts its influence on the homobenzylic position. In the case of anions, field effects and the inductive withdrawal of electron density by the metal are strongly stabilizing. When cations at the homobenzylic position are able to directly interact with

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(20) (a) Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 1545−1546. (b) Richey, H. G., Jr.; Nichols, J. D.; Gassman, P. G.; Fentiman, A. F., Jr.; Winstein, S.; Brookhart, M.; Lustgarten, R. K. *J. Am. Chem. Soc.* **1970**, *92*, 3783−3784. (c) Prakash, G. K. S.; Iyer, P. S. *Rev. Chem. Intermed.* **1988**, *9*, 65−116. (d) Wells, D. K.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1969**, *91*, 5871−5872.

(21) Newcomb, M.; Choi, S.-Y.; Toy, P. H. *Can. J. Chem.* **1999**, *77*, 1123−1135.

(22) Albright, T. A. *Tetrahedron* **1982**, *38*, 1339−1388.

the metal, donation of d orbital electron density is stabilizing. Radicals, however, are essentially unaffected by the presence of a chromium tricarbonyl fragment.

The general conclusion from this and previous studies[3,9] is that the chromium tricarbonyl moiety in arene systems is highly polarizable and thus inductively electron withdrawing, but directly electron donating. Cationic carbon centers preferentially interact directly with the metal center, maintaining an 18-electron configuration yet donating chromium d orbital electrons to the carbon center. Anionic carbon centers do not interact directly with the metal center, though, as such an interaction would result in an unfavorable 20-electron complex. Anionic species are stabilized, however, by field and inductive effects due to the metal or a coordination change such as in the complexed benzyl anion wherein an η^5 geometry localizes the charge on the chromium tricarbonyl moiety.

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Supporting Information Available: Calculated geometries, energies, and Cartesian coordinates for all reported species (compounds **1**−**23**) are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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